Nonlinear Optical Responses of Dialkoxyazobenzene Isomers Adsorbed to Interface between Heptane and Viologen-Modified Quartz Plates[1]

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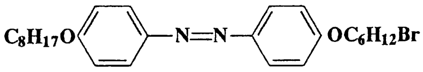
Surface SHG was observed, when a quartz plate with a submonolayer of viologen molecules on the surface was dipped into the heptane solution of 4,4'-dialkoxyazobenzene. Isomerization of the azobenzene moiety from the trans- to cis-form induced large increase in the SHG. The SHG was ascribed to intramolecular charge-transfer from the alkoxy- to the azo group of the non-centrosymmetrically aligned isomers on the quartz plate.

Solid-liquid interfaces provide many interesting subjects to be investigated by SHG techniques.[2] Azobenzene derivatives may be adequate probe molecules for this purpose, since the photoisomerization induces large change in dipole moment and molecular hyperpolarizability.[3] Fujishima and his associates reported variation of SHG signals due to azobenzene moiety embedded in LB films on photo-isomerization.[4] The SHG signal was reported to decrease by ca 20% upon UV irradiation (i.e. isomerization from trans- to cis-isomer). The SHG signals due to an azobenzoic acid derivative at liquid-liquid (water-dichloroethane) interface decreased also on the isomerization to cis-form.[3] Azobenzenes in these studies have two electronically different substituents at the 4- and 4'-positions, which afford large molecular hyperpolarizability due to the contribution of intramolecular charge-transfer along long axis of the molecules. If the two substituents at the 4- and 4'-positions are electronically equivalent, a center of symmetry exists in the π-electron system of the trans-form and the vectorial sum of dipole moment due to the intramolecular charge-transfer becomes null in principle. As for the cis-form, on the other hand, dipole moments due to the intramolecular charge-transfer from the substituted benzene rings to the azo group will add up to afford a component along C_2 axis of the molecule. Then, the molecular hyperpolarizability for the cis-form might dominate over that for the trans-form. Increase in second harmonic light (SHL) intensity on isomerization from the trans- to cis-form could be expected, if the disubstituted azobenzene molecules are non-centrosymmetrically aligned on a surface. This expectation was realized, for the first time, by the use of 4,4'-dialkoxyazobenzene as described below.

The surface SHG was measured with a viologen-modified quartz plate suspended in heptane solutions of the azobenzenes. Remarkable increase in SHL intensity was observed on the formation of the cis-isomer in good contrast to the above quoted two reports.[3,4] Quartz plates (8 × 40 mm, 1 mm thick) were pretreated by KOH-saturated ethanol solution.[5] The plates were then kept dipping in 5×10^{-5} M (M=mol dm^{-3}) methanol solution of ethylcetylviologen (ECV) for 90 min to complete ion exchange, and dried at room temperature. Electronic absorption spectra of the plate indicated that the surface was covered by a submonolayer of the viologen molecules.[6] By the aid of a computer-controlled rotation stage, the ECV-modified quartz plate was suspended in a quartz cell, which contained the heptane solution of the following dialkoxyazobenzene:

1:



The dialkoxyazobenzene was prepared by standard procedures. Experimental procedures and setups for measuring surface SHG were essentially the same as described in our previous paper.[7] Fundamental light (1064 nm) from a Nd:YAG laser (Continuum YG660B-10S, pulse duration 5-6 ns, repetition rate 2-10 Hz) was incident on the quartz plate at various incident angles (θ) with respect to the surface normal. The second harmonic light (SHL) intensity at various θ was measured with p-polarized incident- and emitted light. Clear interference fringe patterns were observed, when surface SHG took place at the front- and back of the quartz plate in heptane solutions of 1.

The isomer ratios of 1 in heptane solutions were adjusted by irradiating light from a high-pressure mercury lamp. The trans-to-cis isomerization was induced by light covering through UV-region down to 340 nm (denoted by Sw), while trans-rich solution was obtained again by successive irradiation of visible light above 400 nm (denoted by Lw).[8] A heptane solution of 1 (2×10^{-4} M) was irradiated in a quartz cell (1 cm optical path), and the isomer ratios were estimated from the electronic absorption spectra. The irradiation for 1 min was long enough for the isomer ratio (trans vs cis) to reach asymptotic values: 29 vs 71% for Sw and 63 vs 37% for Lw, respectively. The Sw-dark-Lw-dark cycles were repeated to confirm the isomer ratios, which remained the same in the dark for more than 30 min.

Effects of the isomer ratios on the surface SHG at the stationary states were examined as the first step. Heptane solutions of 1 in three specific isomer ratios were prepared by photoirradiation before immersing the ECV-modified quartz plates. The surface SHG due to the isomers clearly differed as shown in Table 1, where the SHL intensities with the heptane solutions of 1 in the three isomer ratios are compared. A single ECV-modified quartz plate was commonly used throughout these experiments. After the measurement with each solution, the plate was rinsed in pure heptane to confirm the absence of 1.

Remarkable increase in the SHL intensity was observed with the Sw-irradiated solution. Comparing the SHL intensities and the isomer ratios, one reaches to a conclusion that the SHG due to the cis-isomer is more than 4-times larger in comparison with that of the trans-isomer. This result is in excellent agreement with

Table 1. Variation in SHL intensity with isomer ratios of 1 in the heptane solution as prepared by photoirradiation

Irradiatied light	None	Sw	Lw
cis isomer/%	0	71	37
SHL intensity[a]	40	208	137

[a] The values, in arbitrary units, were obtained from the SHL fringe patterns between 40 and 50° in θ.

our expectation as described in the introduction.

As the second step, dynamic features of the surface SHG was examined by monitoring SHL intensity under the photoirradiation reactions. The light beam from a high-pressure mercury lamp, in perpendicular direction with respect to the laser, irradiated the cell which contained the quartz plate and heptane solution of 1 (2×10^{-4} M). The SHL intensity was measured at a fixed incident angle (θ=45°) with respect to the surface normal. Photoirradiation either with Sw or Lw was carried out for 1 min, each of which was followed by 2 min dark period. The experiments were carried out at 15 ℃ by the use of a thermostatted cell holder. The SHL intensity at θ= 45° was continuously recorded during the irradiation cycle. Figure 1 shows SHL variation with the irradiation cycle, when the solution was initially free from the cis-isomer. The SHL intensity sharply rose on the first Sw irradiation, and remained the same in the succeeding dark period. The SHL intensity was reduced by the Lw irradiation. The photoirradiation effects on the SHL were repeatedly confirmed by the use of Sw-dark-Lw-dark cycles. The SHL intensity changed immediately on the irradiation, and the variation in relative SHL intensity during the irradiation cycle was in good agreement with the data in Table 1. This agreement suggests rapid exchange between the adsorbed compound 1 on the surface and those in the heptane solution.

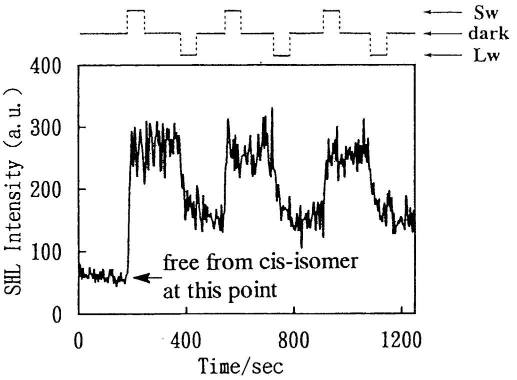
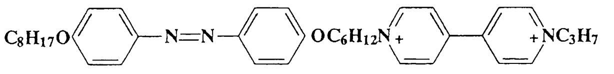


Figure 1. Variation of SHL from ECV-modified plates on photoisomerization of 1 in heptane solution. The intensity at θ= 45° was recorded during Sw-dark-Lw-dark irradiation cycles.

As the third step, the 4,4'-dialkoxyazobenzene unit was electrostatically bound to the quartz surface via viologen moiety of the following linked compound 2:

2:


Analogously to ECV-modification, the quartz plate was kept dipping in ethylacetate solution of 2 for 90 min and dried at room temperature. Electronic absorption due to azobenzene moiety on the plate indicated that the surface was covered by a submonolayer of 2.[9] Clear SHG was observed and the SHL intensity instantaneously varied on the photoirradiation during the Sw-dark-Lw cycles in exactly the same manner as discussed with Figure 1. The SHL intensity ratio between the Sw- and Lw-irradiation experiments were in reasonable agreement with that in Table 1. The optical switching between the bistable states in SHL intensity was finally concluded to represent change in isomer ratios of the dialkoxyazobenzene moiety on the quartz surface.

In the absence of ECV on the quartz plate, no SHG was observed with the heptane solution of 1. On replacing ECV by N-propyl(4,4'-bipyridine) with single positive charge, the surface SHG was still observed but the intensity became considerably weak. The surface SHG could not be detected even with the ECV-modified plate, when either 4-methoxy- or unsubstituted-azobenzene was used in place of 1. Prerequisites for the surface SHG under discussion appear to be two positive charges as in viologen and two alkoxy groups at 4- and 4'-positions of azobenzene moiety. Two other 4,4'-dialkoxyazobenzenes in combination with the ECV-modified plate afforded similar SHL intensity, which varies on photo-irradiation as observed with 1. Presence of dipole moment due to the intramolecular charge-transfer in 4,4'-dialkoxyazobenzenes might be partly responsible to the interaction between viologen and 4,4'-dialkoxyazobenzenes. Possible contribution of charge-transfer interactions between viologen- and 4,4'-dialkoxy-azobenzene moieties to the SHG may be disregarded, since electron-affinity of azobenzene is not far from that of viologen.[10] The viologen moiety may not be directly involved in SHG. It is most likely that the viologen simply establish non-centrosymmetric alignment of the isomer molecules on the surface. The aligned dipoles due to intramolecular charge-transfer from the alkoxy- to azo-group of 4,4'-dialkoxyazobenzenes must be the origin of the SHG under discussion.

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References and Notes

1 Contribution No. 1027 from the Department of Chemical Science and Technology, Faculty of Engineering, Kyushu University.
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6 The surface coverage, as estimated by the method in Ref. 7, was 180 Å^2 per single molecule. The cross section of viologen moiety is 114 Å^2, when space-filling molecular models are applied to lying flat molecules.
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8 Toshiba cut-off filters UV-35 and Y-44B were used to obtain Sw and Lw, respectively.
9 The surface coverage was 98 Å^2 per single molecule (i.e., 86% coverage by the lying flat molecule 2.)
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